RESEARCH ARTICLE

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Investigation of Aggregation Behavior and Molecular Weight Changes of Asphaltene Model Compound

Francis Nsiah, Seth K. Fiafor, and Subir Bhattacharjee

ABSTRACT

We investigate the aggregation of Violanthrone-78 (VO-78), a model asphaltene compound, in mixtures of toluene and n-heptane (heptol) using spectroscopic and dynamic and static light scattering techniques. The light scattering experiments were conducted using pure toluene and n-heptane, as well as 25/75, 50/50, and 75/25 heptol solvents. Furthermore, the concentration of VO-78 varied from 10^{-8} M to 10^{-3} M in these suspensions. The dynamic light scattering experiments were used to study the aggregate sizes from the intensity autocorrelation function at different n-heptane volume fractions. The results show the onset of aggregation of about 50 % n-heptane volume fractions. The aggregate sizes in toluene, within the range of concentrations examined, were below the instrument's detection limit (< 5 nm) but increased with increasing dosages of n-heptane. On the other hand, the aggregate size in pure heptane was observed to be greater than the maximum limit of the instrument (> 10 μm). Furthermore, the static light scattering experiments provided an anomalous behavior. Increasing concentrations of VO-78 in the solvent resulted in lowering the parameter Kc/R_θ, where c is the molar concentration.

Keywords: Aggregation, Asphaltenes, Light Scattering, Violanthrone.

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I. Introduction

Over the past few decades, investigations into the molecular structure of asphaltenes and their analogs have been carried out using various methodologies ranging from simulations to molecular spectroscopic techniques with a view to unraveling the mystery surrounding the asphaltene moiety [1]–[5]. Spectroscopic techniques ranging from Ultraviolet-Visible (UV-Vis) to Mass Spectrometry (MS) have been utilized to elucidate the structure of asphaltenes and their molecular analogs [6]–[8]. The application of these spectroscopic techniques has provided essential structural details which have served as clues to the actual asphaltene structure which has eluded scientists for years. Other techniques such as Gel Permeation Chromatography, Vapour Pressure Osmometry (VPO), X-ray, and neutron small-angle scattering (SANS) [8] have also been employed to deduce the size of polydispersity and the weighted average molecular weight. Most of these techniques require either the adsorption of the sample onto a modified substrate, very dilute asphaltene concentrations, or single solvent systems [5]. Such sample preparation methods may modify the native structure of the asphaltene systems. In some instances, the true colloidal nature of these molecules in natural petroleum environments might be absent in such artificial solvent environments [9].

Asphaltenes are generally soluble in toluene and insoluble in n-heptane [8],[10]–[13]. Hence, mixed solvent systems may reveal structural characteristics of asphaltene aggregates that may not be noticeable in pure/single solvent systems. The work reported herein focuses on the investigation of the aggregation behavior of Violanthrone-78 (VO-78) in a mixed solvent system containing different proportions of n-heptane and toluene (heptol). The structure of VO-78 is shown in Fig. 1 [3],[11],[14]. Simultaneous multiangle static and dynamic light scattering (SMSDLS) was used for the investigation.

Static light scattering (SLS) is a sensitive, non-invasive technique that depends on the measurement of the intensity of light scattered particles as a function of the angle from the transmitted beam [7],[15],[16]. The relationship between light intensity and scattering angle depends on factors such as particle size, shape, refractive index, and size distribution [16]. Consequently, SLS measurements can provide information about all these aforementioned quantities.

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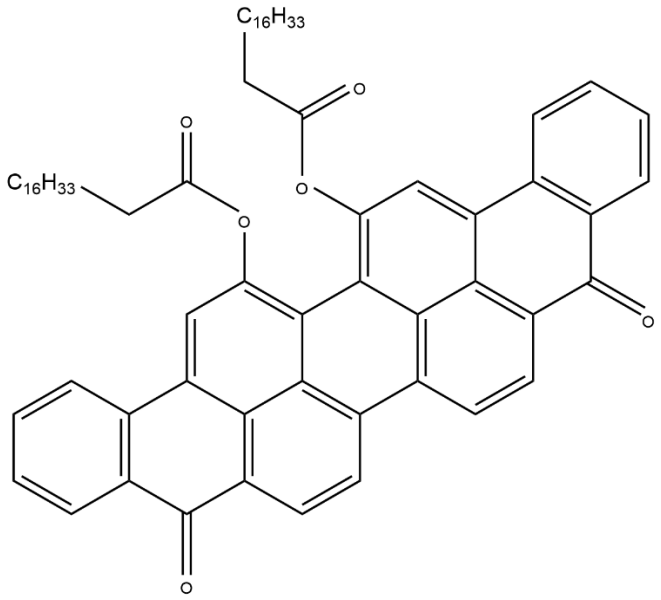

Fig. 1. Structure of Violanthrone-78 (VO-78) showing its functional group compositions.

Dynamic light scattering (DLS), on the other hand, provides the intensity autocorrelation function, which captures the Brownian motion of the suspended entities in a solvent, leading to an estimation of the hydrodynamic radii of these entities. Performing these two light scattering modes concurrently provides a rich set of information regarding the aggregates, including the hydrodynamic dimensions, the molecular weights, and the second virial coefficients [15],[16]. In this paper, we explore the use of this technique on the model asphaltene-like molecule to study its aggregation in different pure and mixed solvents with different levels of aromaticity. More specifically, we aim to relate the propensity of aggregation of these molecules to the degree of solvent aromaticity and their concentration in the solvent.

II. Materials and Methods

A. Reagents and Materials

HPLC grade toluene and n-heptane (Analar grade) were obtained from Fischer Scientific Company (Ottawa, ON) and used as received. All solutions and reagents were filtered on Whatman Anatop 25 (0.02 μm) filters. Violanthrone–78 (VO–78), a model asphaltene compound, was purchased from Aldrich (Milwaukee, WI) and used as received.

B. Asphaltene-Model Compound Sample Preparation

UV–Vis and fluorescence spectroscopic measurements employed Violanthrone–78 (VO–78; C70H84O6; MW = 1021.4) solution concentrations of 10–4 g/mL, 10–5 g/mL, 10–6 g/mL and 10-7 g/mL prepared using HPLC grade toluene as solvent. For the light scattering studies, 1 mM solutions of Violanthrone–78 (VO–78; C70H84O6; MW = 1021.4) were prepared using HPLC grade toluene and n-heptane as solvents. All solutions and reagents were filtered using Whatman Anatop 25 (0.02 μm) filters. Sample solutions were sonicated for 30 min at room temperature using an ultrasonic bath (Elma) equipped with a degasser before analysis to dislodge bubbles and ensure uniform particle distribution within solutions. Refractive indices measured at 23 ± 0.02 ℃ on a Projection Abbe refractometer for 100 % toluene, 100% n-heptane, and 50:50 heptol were 1.4940, 1.3850, and 1.4392 RIU, respectively. These results suggest a linear dependence of the refractive index with n-heptane volume fraction in the mixed solvent system. The mixture was homogenized in an ultrasound bath for 5 min and left to equilibrate. This solution was the stock solution from which other solutions were prepared and diluted to 10–4 g/mL, 10–5 g/mL, 10-6 g/mL, and 10–7 g/mL solutions of VO–78. Solutions were then placed in an ultrasound bath for 5 min to ensure homogeneity. Both filtered and unfiltered solutions were examined to provide insight into the aggregation behavior of each extracted asphaltenes.

C. Spectroscopic Measurements of VO–78 Samples

UV–vis measurements: T70 single-beam spectrophotometer (PG Instrument Ltd., UK), equipped with multi-cell accessories and a dual-source made up of deuterium and tungsten lamps, was used for the UV-vis measurements. The optical absorption spectral range of 200–1100 nm was used in this study. The samples and the reference (toluene) optical cuvettes had a path length of 1 cm. Reproducible results were

obtained with precise absorbance measurements.

Fluorescence measurements: Fluorescence spectroscopic analyses were carried out using Cary Eclipse Fluorescence Spectrophotometer (Varian Inc., Australia) equipped with a xenon lamp. The optical absorption spectral range of 200–1100 nm was used in this study. The samples and the reference (toluene) optical cuvettes had a path length of 1 cm. Fluorescence intensity measurements were reliably reproducible.

Static Light Scattering Measurements: Light scattering measurements were performed on an ALV/CGS-3 Goniometer system (Malvern/ALV-GmbH). The ALV/CGS-3 is a self-contained system with a 22 mW HeNe Laser, an optical fiber-based detector, and a single-photon detector. It simultaneously measures dynamic light (DLS) and static light scattering (SLS). The optical detection has been designed to obtain a significantly higher count rate per mW, leading to reduced measurement times for SLS measurement while not sacrificing DLS accuracy. The goniometer system has a cell-housing index matching vat filled with HPLC grade toluene. The scattering angles studied varied from 60° to 120°. Samples were loaded into a sample tube with each sample run at time intervals of 10, 30, 60, 90, 120, 150, and 180 s at three runs for each specified time. Toluene was used as a reference standard in all measurements.

III. Results and Discussion

A. Spectroscopic Analysis of Violanthrone-78

To obtain a thorough understanding of asphaltene chemistry and a reasonable estimation of spectral characteristics with a model-independent analysis, we chose violanthrone–78 (VO–78), a model asphaltene compound with structural features similar to that expected of asphaltene. Violanthrone is a dye of the quinonoid series used as a model compound for coal and bitumen in carbonization experiments for which its structure is required [9],[11],[14],[17],[18]. Violanthrone–78 and its analogs, such as violanthrone–79 (VO–79) and quinolone–65 (Q65), have been used in the literature for studies on the asphaltene chemistry [10],[14],[17],[19]–[21]. The purpose of this initial stage of our investigation into asphaltene chemistry is to provide a platform that mimics asphaltene structural analysis.

The choice of VO–78 was not only based on its availability and higher solubility in toluene but also on its specific properties similar to compounds present in asphaltene. These include high molecular weight, aromaticity, naphtenicity, heteroatom content, and the nature of its functional groups. Spectral analysis of various violanthrone–78 concentrations of 10–3, 10–4, 10–5, 10–6, and 10–7 g/mL was carried out. The UV–vis spectral analysis of 10–5 g/mL VO–78 within the absorption range of 300–800 nm is presented in Fig. 2. The two absorption peaks observed at positions 535 and 580 nm in Figure 2 are characteristic of porphyrins [20]. The observed wavelength maximum at 580 nm position is consistent with the literature [10],[20],[22]. It confirms the absorption of radiation in the porphyrin-type compounds and organic dyes [3],[23],[24]. The appearance of these peaks within this spectral region suggests that asphaltene UV–Vis absorption is significant in the range of 450 to 650 nm.

Additional spectroscopic investigation into the fluorescence behavior of violanthrone–78 was undertaken to gain insight into its structural characteristics further. In spectral analysis, since excitation is a mirror image of emission, it is always prudent to use the wavelength corresponding to the highest excitation peak for further fluorescence emission studies. Thus, Fig. 3 shows a fluorescence emission spectrum of a diluted solution of VO–78 obtained with a 580–nm excitation wavelength. This spectrum represents the overlapping spectra of the many chromophores contained within the VO–78 molecules [20],[25],[26]. The observed emission wavelength maximum occurred at 635 nm, characteristic of VO–78 [12],[20],[27].

With changes in-ring location and substitution [20],[28],[29], there is bound to be some change in the spectral position of the fluorescence emission maximum. Nonetheless, the wavelength of fluorescence emission does correlate with chromophore size.

Although, it is difficult to use the fluorescence emission spectrum to obtain an exact distribution of ring sizes since optical absorption and emission constants are different for different chromophores. However, these differences in the optical constants are somewhat canceled to some degree because the smaller transition strengths in smaller aromatics are offset by their larger quantum yields. Hence, estimating the range of the size of asphaltene based on its VO–78 model compound is reasonable.

It is also our belief that subtle changes in a molecule may be revealed through different fractions and concentrations of the molecule. Hence, the need to examine the fluorescence spectra of VO–78 taken at different concentrations, as demonstrated in Fig. 3.

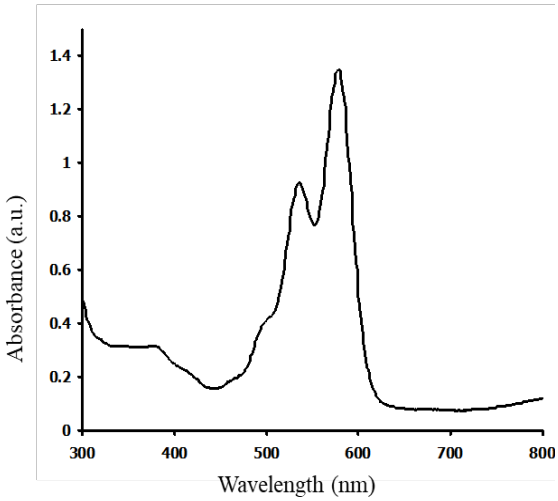

Fig. 2. UV–Vis spectrum of violanthrone–78 showing absorption maximum at 580 nm.

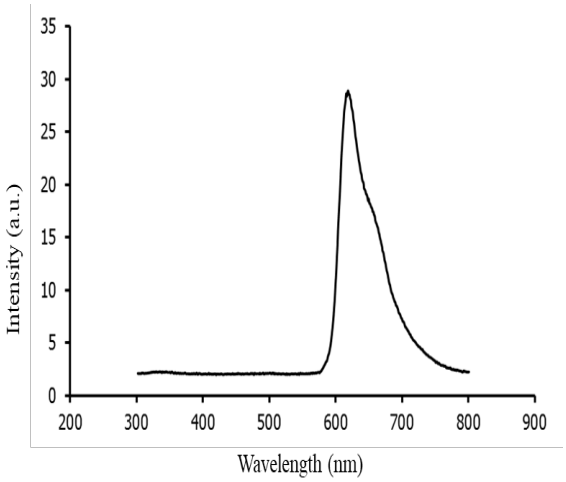

Fig. 3. Emission spectrum of violanthrone–78 showing emission maximum at 635 nm.

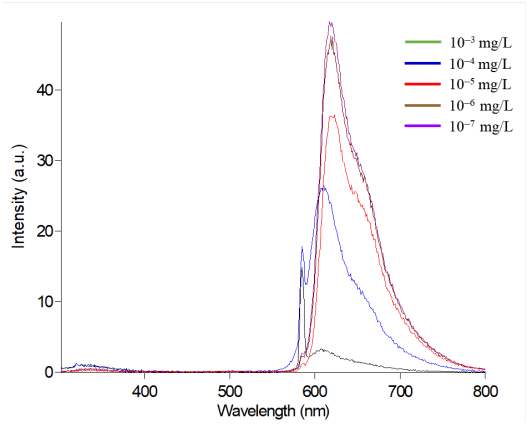

Fig. 4. Emission spectra of different violanthrone–78 showing emission maximum at 635 nm.

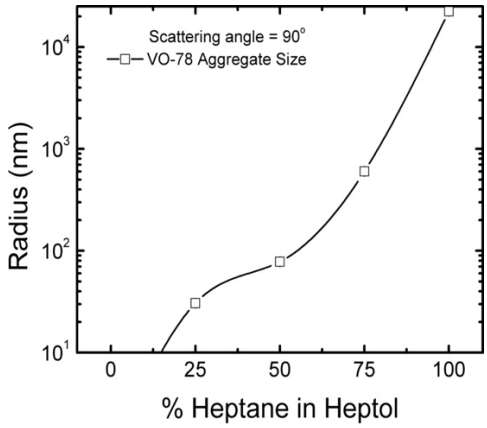

Fig. 5. Plot showing aggregation behavior of VO–78 in varying heptol concentrations at a scattering angle of 90°.

In Fig. 4, there are the fluorescence spectra of VO–78 taken at different concentrations of 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}, and 10^{-7} g/mL. It was observed that the variations in the fluorescence intensities with concentration are consistent with Beer-Lambert's law. Therefore, a peak around 590 nm may be attributable to a fluorescent impurity in the sample [10],[20]. However, its true origin can be explained within the limits of the spectroscopic tools employed in this study. Again, a tiny shoulder emerges on the higher wavelength region of the peaks, particularly at higher concentrations. Applying more detailed structural elucidation tools such as NMR and mass spectrometer may help unravel the identity of this shoulder.

Nevertheless, Mullins and co-workers have used both UV–Vis absorption and fluorescence emission spectra within the spectral region employed in their study to estimate the number of fused rings [12],[13], [22]. Hence, it is believed that using a known chromophore (VO–78), the molecular weight and structural characteristics of asphaltene can be estimated [10],[12],[20]. Furthermore, a strong correlation could be established between chromophore size and the molecular size (weight) of the asphaltene moiety based on its origin. Besides, there is limited study in the literature on the hydrodynamic radius of VO–78. Hence, it is necessary to expand the scope of our study to cover the hydrodynamic radius and aggregation behavior of VO–78 in a mixed solvent.

B. Hydrodynamic Radius–DLS Measurements

Asphaltenes are generally soluble in toluene and insoluble in n-heptane [3],[13],[24]. Hence, mixed solvent systems may reveal structural characteristics of asphaltene aggregates that may not be noticeable in pure/single solvent systems. This aspect of the study presented herein looked further into the aggregation behavior of Violanthrone–78 (VO–78) in a mixed solvent system containing different proportions of n-heptane and toluene (heptol). A simultaneous multiangle static and dynamic light scattering (SMSDLS) was used for the investigation. The extent of aggregation was examined using dynamic light scattering. Fig. 5 plots the measured hydrodynamic radius of the VO–78 aggregates obtained at different proportions of n-heptane in the heptol solvent system. The hydrodynamic radii were measured at a scattering angle of 90°.

The measurements were reported from a VO–78 concentration of 1 mM. The plot reveals that the onset of aggregation of the asphaltene–like molecules in heptol occurs above ca. 25 % volume percent of n-heptane, and the aggregate hydrodynamic radius continues to increase as the heptane volume fraction is increased. The particle size for pure toluene was below the instrument's detection limit.

For pure heptane, on the other hand, the reported aggregate size was found to be much larger than the upper limit of a size that can be determined using light scattering. Each VO–78 molecule is reasonably large, with a polyaromatic ring system that can undergo π-π stacking and hydrophobic interactions in a less polar solvent like n-heptane. These molecules did not form an aggregate in toluene over the studied range of concentrations. The extent of aggregation increases slowly with an increase in the percentage of n-heptane. Thus, the work presented in this section has revealed novel aggregation behavior, which opens the door to further developments into the aggregation behavior of asphaltenes. It further shows the potential of dynamic and static light scattering techniques in probing asphaltene surrogates.

C. Static Light Scattering

The molecular weight dependence on both heptol concentration and scattering angle was probed using static light scattering between 60° and 120°. Fig. 6 shows a Zimm plot of VO–78. A Zimm plot of our data revealed a trend contrary to what one would have observed from a typical trend of increasing concentration with a concomitant increase in KC/R values [15],[16],[30]. We could not obtain a 1/Mw value by simple extrapolation. This observation was not an anomaly but showed a unique event regarding monomeric entities of the VO–78 molecule [10],[11],[17]. At low concentrations, there is less interaction between the monomer units. However, increased concentration results in a concomitant effect of a greater repulsion between the monomer units leading to a high degree of dissociation within the asphaltene model compound. Further studies will be required using other model compounds and known polymeric molecules to understand this trend entirely.

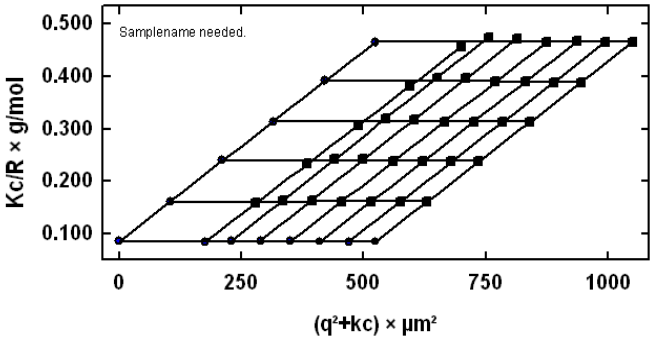

Fig. 6. Zimm plot showing aggregation behavior of VO–78 in varying heptol concentrations at a scattering angle of 60° to 120°.

IV. CONCLUSION

The work presented in the paper reveals novel aggregation behavior, which opens the door to further developments into the aggregation behavior of asphaltenes. Light scattering may serve as a means of systematically assessing the aggregation behavior and dynamics of asphaltenes and, consequently, the role of such molecules in the extraction and upgrading of bitumen and heavy oil. It further shows the potential of dynamic and static light scattering techniques in probing asphaltene surrogates.

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CONFLICT OF INTEREST

The authors declare that they do not have any conflict of interest.

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